

# ALLYL ETHER OF STARCH

## Preparation and Industrial Possibilities

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Soluble allyl ether of starch has been prepared from starch acetate and also by direct allylation of starch. The compound is oxidized and polymerized to an insoluble and infusible product. Heat and paint driers accelerate the polymerization. Possible industrial uses of allyl starch as coatings, adhesives, and plastic intermediates are discussed.

THE only reference to allyl starch in the literature is that by Tomecko and Adams (3), who prepared what they called a "monoallyl starch" by direct substitution of starch with allyl bromide in the presence of 10% aqueous potassium hydroxide. The product had 0.5 allyl group per glucose unit. Repetition of the experiments of Tomecko and Adams gave a white amorphous powder, slightly soluble in water and practically insoluble in acetone, ethylene chlorohydrin, and other organic solvents, with 0.5 allyl group per glucose unit. This was similar to the substance obtained by Tomecko and Adams. They determined the degree of substitution by combustion analyses. We used the same method for insoluble compounds and the Wijs method for compounds soluble in organic solvents. Slight modifications in the concentrations of starch, alkali or allyl bromide or in the reaction time did not affect the composition of the final product.

A clue to the explanation of low substitution in the product obtained by Tomecko and Adams was found in the fact that no allyl bromide could be recovered in spite of the large excess used (85 to 10 grams starch or a mole ratio of 11 to 1). This was attributed to two side reactions which parallel the main reaction of etherifying the hydroxyl groups. The allyl bromide is hydrolyzed by the alkali to allyl alcohol, and this reacts with allyl bromide to form allyl ether. The hydrolysis of allyl bromide and also of allyl chloride (used in later experiments) at various temperatures and with various concentrations of alkali was therefore investigated. Equal volumes of allyl bromide or chloride and sodium hydroxide solution were mixed and stirred at various temperatures for 3 hours. At 80° C. (approximately the temperature of the reaction for the preparation of allyl starch) the results were as follows: With alkali concentrations up to 10%, about 23% of allyl bromide was hydrolyzed<sup>1</sup>; with 20 to 30% alkali, about 9%; and with 40 to 50%, only about 2.5%. About 21% allyl chloride was hydrolyzed with 10% sodium hydroxide, and only about 1% with 40 to 50% alkali.

These experiments pointed to the advisability of using higher concentrations of alkali in the preparation of allyl starch. As a matter of fact, when concentrated alkaline solutions were used, with the same excess of allyl bromide, compounds of a higher degree of substitution (up to 2.6 allyl groups per glucose molecule) were obtained, and a considerable amount of allyl bromide could be recovered after

the reaction was complete. The powdery product thus obtained was infusible and insoluble in all organic solvents tested.

It appears that allyl ether of starch insolubilizes with greater ease than the comparatively easily oxidizable allyl ethers of simpler carbohydrates (2).

### METHODS OF PREPARATION

On the assumption that easily oxidizable allyl starch might be more stable in solution, we adopted a method similar to that used by Haworth, Hirst, and Webb (1) for methylation of starch—that is, simultaneous hydrolysis and allylation of starch acetate in acetone solution. This method, which does not require an autoclave, is carried out as follows: In a flask fitted with a mechanical stirrer and reflux condenser, 100 grams of starch acetate are dissolved in 250 cc. of acetone; 250 grams of 50% aqueous sodium hydroxide and 300 cc. of allyl bromide are added, and the mixture is heated at reflux temperature for 3.5 hours. The volatile portion of the reaction mixture is then removed rapidly (15 minutes) by distillation with steam, the gummy product remaining in the flask is washed until alkali-free, and it is then dissolved in about 150 cc. of acetone. When this acetone solution is poured into rapidly stirred water at room temperature, nearly white gummy allyl starch is obtained. The yield is about 90 grams of the gum, containing about 20% of water. An appreciable proportion of the allyl bromide used can be recovered from the steam-distilled liquid.

The same compound can be prepared with allyl chloride, which is cheaper. But for this reaction heating in an autoclave at 80° C. for about 11 hours is required.

For producing larger quantities of allyl starch, the following method is more economical: Five hundred grams of air-dry starch is stirred into 2000 grams of 50% aqueous sodium hydroxide in an autoclave at room temperature, and 2500 cc. of acetone and 3000 cc. of allyl chloride are added with constant stirring. The autoclave is heated at about 86° C. (approximately 30 pounds pressure). The liquid is then distilled with steam for about 40 minutes to remove the acetone and excess of allyl chloride. The separated gum is washed with water until free of alkali. The gum can be further purified by dissolving in acetone, filtering off the small amount of unchanged or lowly substituted starch (less than 3%), and precipitating with water. Acetone, allyl chloride, and allyl ether can be recovered from the distillate. The results of several runs are given in Table I. They were ob-

TABLE I. PREPARATION OF ALLYL STARCH

Material Used	Moisture	Reaction Time, Hr.	Yield, Grams	Yield Cor. for Moisture of Product, %	Yield, % of Theoretical	% Allyl Content (Wijs Method)	Allyl Groups per Glucose Unit	Grams Recovered	
								Allyl chloride	Allyl ether
Potato starch	16	11	860	612	93	37.0	2.3	795	94
Potato starch	16	11	890	620	94	37.1	2.3	1213	79
Sweet potato starch	14	10	900	603	99	30.0	1.7	924	117
Cornstarch	12	10	986	684	98	37.4	2.4	770	72
Cornstarch	12	10	972	676	96	37.5	2.4	882	105
Tapioca starch	13	9	830	617	92	35.0	2.1	823	93
Waxy maize starch	10	20	900	617	92	33.5	2.0	460	68
Standard tapioca dextrin <sup>a</sup>	3	4	816	846	89	33.2	2.0	1262	89

<sup>a</sup> Viscosity, 8.5 centistokes in 50% solution at 130° F.

<sup>1</sup> At concentrations up to 10%, the entire amount of alkali was used up, and therefore 23% represents the minimum hydrolyzed.

tained with the laboratory equipment available and do not represent the optimum yields and recovery of solvent.

This table shows that for most ordinary starches the reaction time is about 10 hours; for waxy maize starch, which consists entirely of amylopectin, it is 20 hours; for a starch-degradation product such as dextrin, it is 4 hours. The percentage of allyl in the product decreases somewhat with time, owing to the slow oxidation and polymerization of allyl starch, even at room temperature or below. The yields are given on a wet basis (20–25% moisture).

No attempt was made to recover the acetone from the steam distillate, which was washed with water and then fractionated to recover the allyl chloride and allyl ether. Perhaps in commercial practice the mixture of allyl chloride and acetone could be used for making the next batch.

#### PHYSICAL AND CHEMICAL PROPERTIES

Allyl starch prepared by these methods is a soft, gummy (but not tacky) material containing about 2 allyl groups per glucose unit. Products of lower or higher allyl content can be obtained, but they are either powdery or extremely sticky. The powdery form, due to a larger surface exposed, is much less stable. When left in the air, the gummy allyl starch becomes coated with a hard insoluble material, but this can be avoided by keeping the allyl starch under water at a comparatively low temperature. It is soluble in most organic solvents but not in aliphatic hydrocarbons. Solutions of allyl starch in acetone, alcohol, and other solvents are stable. Even a 30% solution has low viscosity. One of the methods for the purification of allyl starch is precipitation from alcohol or acetone solutions with water.

The tendency of the powdery product to become insoluble on exposure to air and the formation of an insoluble coating on the gummy product are apparently due to oxidation and the subsequent cross-linkage polymerization of the partly oxidized compounds. This process can be studied quantitatively on thin films of allyl starch deposited from solutions on surfaces of wood, glass, or metal. On exposure to air, these films gradually become insoluble. The process of insolubilization can be catalyzed by heat, chemical agents, and infrared and ultraviolet radiation.

Quantitative results on insolubilization of films (obtained by Esther M. Terry of this Laboratory) for a number of different preparations of allyl starch at different temperatures, both in the presence and in the absence of a catalyst, are given in Table II. Results obtained at room temperature are shown in Table III. The amount of drier is expressed as per cent by weight of metal (cobalt) on the basis of dry allyl starch. Table II shows that the process of insolubilization proceeds faster at higher temperatures. Addition of catalyst decreases the time required for insolubilization, although the effect is not equally marked in all cases. Infrared or ultraviolet radiation has a marked catalytic effect. The effect of cobalt naphthenate was striking in experiments at room temperature (Table III).

Preliminary experiments have shown that a large percentage of resins and plasticizers are compatible with allyl starch.

#### INDUSTRIAL POSSIBILITIES

Properties of allyl starch suggest that it may be used for various purposes. When dissolved in ordinary lacquer solvents, it can be utilized as a protective and decorative coating for wood, glass, metal, and other surfaces. Because of its high resistance to various solvents, solutions of acids and alkalis, and heat, it should be valuable as a lacquer and varnish for household and office furniture and numerous other articles in everyday use. Several manufacturing concerns are now testing it for these purposes.

It can be used for coating and impregnating paper and textiles, and it acts as a thermosetting adhesive suitable for preparation of laminated products.

Allyl starch can also be used for the preparation of rigid plastics. When compounded on a rubber mill with various ingredi-

TABLE II. INSOLUBILIZATION OF ALLYL STARCH FILMS, WITH AND WITHOUT COBALT NAPHTHENATE

Sample No.	Drier, % Co	Temp., °C.	Type of Heating	% Insoluble Material after:					
				1 hr.	2 hr.	3 hr.	4 hr.	5 hr.	6 hr.:24 hr.
1	...	120	Oven	100	...	...	...	...	...
2	...	120	Oven	100	...	...	...	...	...
3	...	100	Oven	86	94	99	100	...	...
	0.4		Oven	93	93	95	96	97	97
	0.2		Oven	87	93	...	100	...	...
	0.4		Infrared	78	97	99	100	...	...
	0.2		Infrared	91	95	100	...	...	...
4	...	100	Oven	80	89	96	98	100	...
	0.4		Oven	95	96	99	100	...	...
	0.2		Oven	95	95	100	...	...	...
	0.4		Infrared	91	96	100	...	...	...
	0.2		Infrared	89	97	100	...	...	...
5	...	100	Oven	86	95	97	98	100	...
	0.4		Oven	88	92	92	97	...	100
	0.2		Oven	91	92	94	97	99	100
	0.4		Infrared	88	95	100	...	...	...
	0.2		Infrared	89	92	94	97	100	...
6	...	100	Oven	83	95	99	99	100	...
	0.4		Oven	93	93	95	100	...	...
	0.2		Oven	91	92	92	100	...	...
	0.4		Infrared	89	97	100	...	...	...
	0.2		Infrared	92	96	100	...	...	...
7	...	80	Oven	...	79	81	83	88	100
	0.4		Oven	...	92	95	95	99	100
	0.2		Oven	...	94	95	96	99	100
	0.4		Infrared	...	87	94	97	98	100
	0.2		Infrared	...	92	97	98	99	100
8	...	80	Ultraviolet	...	96	100	...	...	...
	0.4		Ultraviolet	...	91	99	100	...	...
	0.2		Ultraviolet	...	92	95	96	96	...
	0.4		Oven	...	79	87	88	94	96
	0.2		Oven	89	90	93	...	94	97

TABLE III. INSOLUBILIZATION OF ALLYL STARCH FILMS AT ROOM TEMPERATURE

Sample No.	Drier, % Co	% Insoluble Material after:			
		1 week	2 weeks	3 weeks	4 weeks
9	...	55	73	73	77
	0.4	91	99	99	100
	0.2	94	96	99	99
10	...	16	...	70	73
	0.4	99	100	...	...
	0.2	99	100	...	...
11	...	...	...	80	82
	0.4	98	100	...	...
	0.2	98	100	...	...
12	...	13	54	72	76
	0.4	98	100	...	...
	0.2	97	100	...	...
13	...	73	77	80	81
	0.4	88	100	...	...
	0.2	91	99	99	100

ents, including sulfur and vulcanization accelerators, and "vulcanized" in a press, the gummy material forms a rigid plastic which is highly resistant to various solvents and other chemical reagents. The milled product, when placed between layers of wood, paper, or cloth, and heated under pressure, yields laminated materials of various degrees of strength and usefulness.

The compatibility of allyl starch with various resins and plasticizers indicates that it may be modified to suit certain specific requirements. Allyl starch can be copolymerized with simpler allyl carbohydrates and other monomeric substances.

#### LITERATURE CITED

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- (3) Tomecko and Adams, *ibid.*, 45, 2698 (1923).